

PREDICTION OF MERCURY AIR EMISSIONS FROM COAL-FIRED POWER PLANTS

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KEYWORDS: mercury, hazardous air pollutants, coal-fired power plant

INTRODUCTION

A recent report by the Environmental Protection Agency (EPA) on emission of hazardous air pollutants by electric utilities predicted that emissions of air toxics from coal-fired utilities would increase by 10 to 30% by the year 2010.¹ Mercury from coal-fired utilities was identified as the hazardous air pollutant of greatest potential public health concern. Anthropogenic emissions of mercury account for 10 to 30% of the world-wide emissions of mercury.² EPA has estimated that during the period 1994-1995 annual emissions of mercury from human activities in the United States were 159 tons.² Approximately 87% of these emissions were from combustion sources. Coal-fired utilities in the U.S. were estimated to emit 51 tons of mercury per year into the air during this period.

The form of mercury emitted from point sources is a critical variable in modeling the patterns and amount of mercury deposition from the atmosphere.^{1,3} Both elemental and oxidized mercury are emitted to the air from combustion point sources. Elemental mercury has a lifetime in the atmosphere of up to a year, while oxidized forms of mercury have lifetimes of a few days or less⁶ as a result of the higher solubility of Hg^{+2} in atmospheric moisture. Elemental mercury can thus be transported over long distances, whereas oxidized and particulate mercury deposit near the point of emission. Once mercury has deposited on land or water, it can transform into methylmercury, an organic form, and thereby enter the food chain. Humans are most likely to be exposed to methylmercury through consumption of fish.

Measurements of the concentration of mercury species taken in the stacks of pilot and full scale coal combustion systems show more than half of the vapor phase mercury as an oxidized form which is likely to be HgCl_2 . Current measurement methods cannot identify specific oxidized species of mercury.^{4,5} The range of observed values is broad: one study consisting of mercury speciation measurements from fourteen different coal combustion systems reported anywhere from 30% Hg^{+2} to 95% Hg^{+2} upstream of the air pollution control device (APCD).⁴

Although we can identify the major reaction pathways for mercury in coal combustion flue gas with some degree of confidence, we cannot yet make quantitative predictions of the emissions of specific mercury species from coal-fired power plants. The goal of this work is to advance the state of knowledge such that a predictive model for emissions of total mercury and for speciation of mercury can be formulated.

MERCURY EMISSIONS

A simple mass balance model for emissions of mercury from coal-fired power plants was devised to test our current understanding of mercury transformations in flue gas. The post-combustion region of the boiler was divided into three parts: 1) convective section to air heater (AH); 2) electrostatic precipitator (ESP); and 3) flue gas desulfurization unit (FGD). Concentrations of mercury species (gaseous and condensed) in each section were either calculated from equilibrium or plant parameters, or assigned based upon limited observations available from field data. All of the mercury is assumed to start as gaseous elemental mercury (Hg^0). In the AH section, elemental mercury can oxidize to Hg^{+2} , nominally the sum of HgO and HgCl_2 . In addition, both Hg^0 and Hg^{+2} can be adsorbed on particulate matter in the AH section, converting them to Hg_p . No change of mercury speciation or partitioning was calculated in the ESP because there are not enough data available to deduce mechanisms (or clear trends). In the FGD section, both Hg^0 and Hg^{+2} can be absorbed into the scrubber solution. In addition, a fraction of the adsorbed Hg^{+2} can be converted to gaseous Hg^0 . The model therefore predicts the speciation and emissions of mercury from the boiler based upon coal mercury content, equilibrium at elevated temperatures, assumed mercury partitioning coefficients in the various sections of the boiler, and scrubber operation as outlined in Table 1.

Recent DoE-sponsored field studies have been conducted to measure mercury speciation and mercury mass balances on coal-fired power plants using the Ontario Hydro method for gaseous mercury sampling. These data provide the best set for testing the model. In one study,⁸ six

power plants were sampled which all burned Eastern bituminous coal. The plants all had wet scrubbers and ESP's. In another study,⁹ a power plant burning a Western lignite was sampled. This plant also had a wet scrubber and an ESP.

Table 1. Mercury Model Parameters

Parameter	Value	Notes
Fraction of Hg^0 Oxidized in AH	**	Calculated from Equilibrium at 825 K
Fraction of Hg^0 Adsorbed in AH	0%	Assumed
Fraction of Hg^{+2} Adsorbed in AH	**	Calculated from LOI for bituminous coals
Fraction of Hg^0 Oxidized in ESP	0%	Assumed
Fraction of Hg^0 Adsorbed in ESP	0%	Assumed
Fraction of Hg^{+2} Adsorbed in ESP	0%	Assumed
Collection Efficiency of ESP	**	Input from Plant Operation
Fraction of Hg^0 Absorbed in FGD	0%	Assumed
Fraction of Hg^{+2} Absorbed in FGD	**	Calculated from scrubber type and operating parameters
Fraction of Adsorbed Hg^{+2} Reduced to Hg^0 in FGD	**	Calculated from scrubber type and operating parameters

Since there is not currently enough information on the gas-phase reactions of mercury in flue gas, a simple approach was taken to predict the amount of mercury oxidation that takes place in the convective pass. When detailed kinetic information is available, this will be incorporated into the model. The amount of oxidation was calculated assuming that the chemical composition is frozen, equal to the equilibrium composition at 825 K. The results of equilibrium calculations at 20% excess air for a number of different coals were used to derive this correlation, shown in Figure 1. A range of chlorine contents, from 25 to 4500 ppm, were used in the calculation. At very low chlorine contents (< 50 ppm), most of the gas-phase oxidized mercury is predicted to be HgO . Many western fuels fall into this low-chlorine category. The adsorption behavior of HgO on fly ash may be different from HgCl_2 .

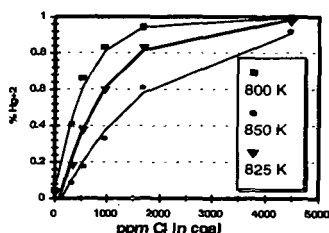
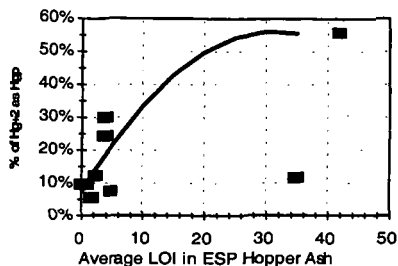


Figure 1. Predicted percentage of oxidized Mercury as a function of coal chlorine content.

At this time, it is not possible to generalize and conclude that high carbon in ash will always give high levels of particulate-bound mercury. However, in the case of similar coals, there may be a relationship as illustrated in Figure 2. The figure shows mercury measured in the ash, as sampled directly from the flue gas using the Ontario Hydro method, for nine different bituminous coals, all from the Northern Appalachian or Illinois Basins. The data were taken either at full scale power plants⁸ or at a large pilot scale unit.⁷ For these coals, there is a relationship between carbon content of ash (as measured by loss-on-ignition) and mercury content. However, the coals represented in the data are all very similar. Data will have to be obtained from a wider range of bituminous coals in order to generalize this relationship.

Western sub-bituminous coals produce fly ash which is very high in calcium. In some cases, ash from these coals has been observed to adsorb large amounts of mercury in the particulate collection device.¹⁰ Calcium silicate sorbents also adsorb mercury chloride.¹¹ However, western coals are generally low in chlorine and produce very little mercury chloride. Some

component of the ash from these coals appears to adsorb elemental mercury. At this time, the mechanism by which elemental mercury is removed by the ash from western sub-bituminous ash is not known.



The majority of utility plants use an electrostatic precipitator (ESP) for particulate control; approximately 10 per cent use a fabric filter or baghouse instead. In the laboratory, fly ash has been observed to act as a catalyst for oxidation of elemental mercury.¹² In other laboratory work,¹³ oxidized mercury has been observed to desorb from carbon-based sorbents and this may also occur for mercury adsorbed on fly ash in particulate control devices.^{7,9}

Figure 2. Mercury content of ash sampled at ESP inlet as a function of loss-on-ignition (LOI) of ESP hopper ash for nine different bituminous coals (References 7 and 8)

Much of the discussion of adsorption of mercury by ash in the convective section applies to the behavior of mercury in the particulate control device. Unfortunately, little recent data on the removal of mercury species across ESPs and baghouses exist. (Older data taken with EPA Method 29 have been shown to speciate mercury incorrectly.) In a pilot scale study conducted by McDermott Technologies and involving combustion of three different Ohio bituminous coals,⁷ gas-phase elemental mercury was removed by both a baghouse and an ESP, while oxidized mercury increased across both devices. This was also observed in a full scale power plant burning a North Dakota lignite.⁹ As mentioned previously, ash from certain western sub-bituminous coals has been shown to remove elemental mercury from flue gas, particularly at lower temperatures.¹⁴ Higher amounts of removal have been observed in baghouses relative to ESPs.

Since there are not enough data on the removal of mercury species across particulate control devices, no correlations have been developed for the preliminary model. Once a larger set of data has been assembled, it may be possible to derive relationships that take into account temperature, coal type, and particulate control device type.

A portion of the mercury may be adsorbed on the fly ash at the inlet to the particulate control device.^{7,12} Combustion of bituminous coals can result in unburned carbon which has been suggested to adsorb mercury. Mercury has been found to concentrate in the carbon-rich fraction of fly ash.¹⁵ Preliminary experimental work on adsorption of gaseous mercury on coal char¹⁶ showed that $HgCl_2$ was adsorbed more efficiently than Hg^0 , with two to fifty times more $HgCl_2$ adsorbed than Hg^0 under the same conditions, and the adsorption of the former was correlated with char surface area. This would also indicate that adsorption of $HgCl_2$ is a physical adsorption process. Adsorption of elemental mercury depended on the rank of the coal from which the char was derived. These results suggest that the nature of the unburned carbon, in terms of morphology and surface chemistry, strongly affects mercury adsorption.

Recent sampling campaigns on full scale utility boilers^{8,9} and a large pilot scale unit⁷ have provided data on the speciation of mercury before and after the FGD. Scrubbers have been observed to efficiently remove oxidized mercury, but not elemental mercury. Based on a detailed study of the behavior of mercury in a pilot scale wet scrubber,⁷ the adsorption of oxidized mercury appears to be strongly correlated with the mass transfer in the scrubber. The liquid-to-gas ratio (L/G) was a good indicator for the amount of Hg^{+2} removed by the scrubber. The composition of the scrubber liquid and design of the scrubber are also important in determining the removal of Hg^{+2} and the nature of the scrubbing solution must be known in order to model mercury removal.

Pilot scale data have been taken on the effect of scrubber slurry pH on mercury removal in limestone scrubbers.⁷ These suggest that the type of scrubber and the L/G ratio, not the pH, are the two key variables for modeling adsorption of Hg^{+2} across FGDs. Under some conditions, limestone scrubbers have been observed to reduce adsorbed mercury back to Hg^0 giving rise to higher concentrations of elemental mercury at the outlet than at the inlet. Assuming that no Hg^0

is adsorbed by the scrubber, the amount of adsorbed Hg^{+2} that is reduced can be calculated from the ratio of the increase in elemental mercury to the decrease in Hg^{+2} across the scrubber. Based on very limited data, this also appears to be related to the L/G ratio in the scrubber, although the effect is slight.

Figures 3 and 4 show a comparison of the measured and calculated values for mercury speciation (denoted by the fraction of mercury as Hg^{+2}) and total mercury emissions from the stack, respectively. The model predicts the stack emissions very well ($r^2=0.94$). Although the model is simple in its current form, it also predicts speciation well ($r^2 = 0.59$) using only limited information about the coal composition and operation of the air pollution control equipment. The model is able to predict a range of speciation from less than 5% Hg^{+2} to more than 30% Hg^{+2} .

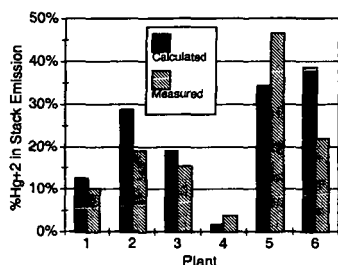


Figure 3. Predicted vs. measured stack speciation.

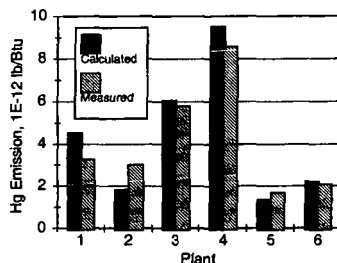


Figure 4. Predicted vs. measured emissions of mercury.

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